

NOTICE: When government or other drawings, specifications or other data are used for any purpose other than in connection with a definitely related government procurement operation, the U. S. Government thereby incurs no responsibility, nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use or sell any patented invention that may in any way be related thereto.

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE;
DISTRIBUTION UNLIMITED.

UNCLASSIFIED

AD **43736**

*Reproduced
by the*

ARMED SERVICES TECHNICAL INFORMATION AGENCY
ARLINGTON HALL STATION
ARLINGTON 12, VIRGINIA



DECLASSIFIED
PER AUTHORITY
TAB **461-2-5**
DATED **JUNE 61**

UNCLASSIFIED

ONR NITROPOLYMER RESEARCH
Contract Nonr-1205(00)

April 1 - June 30, 1954

Report No. Q-10

Copy No. 52

**NOTICE: THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE
NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING
OF THE ESPIONAGE LAWS, TITLE 18, U.S.C., SECTIONS 793 and 794.
THE TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN
ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.**

CONFIDENTIAL

COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

TELEPHONE CRAWFORD 7071

IN REPLY REFER TO -

July 9, 1954
Copy No. 52

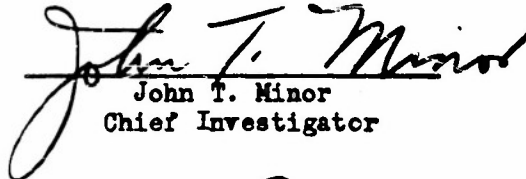
Report No. Q-10
(Quarterly Summary)

SUBJECT: ONR Nitropolymer Research

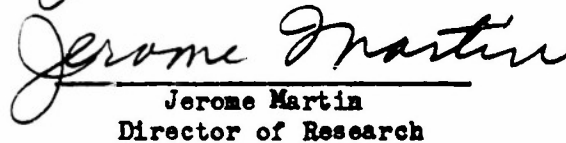
CONTRACT: Nonr-1205(00)

PERIOD April 1, 1954 to
COVERED: June 30, 1954

WRITTEN
BY:


John T. Minor
Chief Investigator

APPROVED
BY:


Jerome Martin
Director of Research

This document contains information affecting the national defense of the United States within the meaning of the Espionage Laws, Title 18, U.S.C., Sections 793 and 794. The transmission or the revelation of its contents in any manner to an unauthorized person is prohibited by law.

CONFIDENTIAL

55960

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10

TABLE OF CONTENTS

	<u>Page</u>
Contract Fulfillment	iii
I. SUMMARY	1
II. TECHNICAL PROGRESS	1
A. Dinitropropyl Acrylate	1
1. Discussion	1
2. Experimental	2
B. Oxidizing Agents	3
C. Dinitrobutyl Acrylate	3

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10

CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of
Contract Nonr-1205(00).

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10

I. SUMMARY

A. This quarterly report is the fourth under Contract Nonr-1205(00) and covers the period from April 1, 1954 to June 30, 1954. The object of the contract is: Conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the applications of processes not now employed in the preparations.

B. The more important results and conclusions of the work of the quarter are presented below.

1. Using pilot plant dinitropropanol (DPL), acrylic acid, and poly phosphoric acid in the preparation of dinitropropyl acrylate (DNPA), it is difficult to control premature polymerization.

2. When toluene is used to prepare DNPA from pilot plant DPL and acrylic acid in poly phosphoric acid, trouble is encountered in obtaining good yields of monomer that will mass polymerize to a soluble product.

3. Good yields of 2-nitro-2-nitrosopropane can be prepared using ferric ion instead of silver ion in the oxidative nitration procedure.

II. TECHNICAL PROGRESS

A. DINITROPROPYL ACRYLATE

1. Discussion

We have studied the preparation of dinitropropyl and commercial acrylic acid in a poly phosphoric acid medium. The initial runs were made to check conditions for obtaining good yields. These were far from the 85 and 94% reported (1). The runs in Table I were made with dinitropropanol prepared in the pilot plant except as noted. This material was the same as we had used in preparations using acrylyl chloride to produce DNPA that polymerized to a soluble polymer. Two different samples of poly phosphoric acid were used. From the results of these runs, one would have to conclude that the chances of having esterification in this strong solvent without premature polymerization were small when our pilot plant DPL is used. This observation has been confirmed on a pilot plant scale (1). When toluene or benzene was used to dissolve the DPL and left in or removed from the reaction mixture, little trouble was encountered with polymerization. Also, these data show the difficulty in obtaining a soluble polymer from the monomer as we were able to prepare it.

1. L. Smith, private communication.

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10

Page 2

2. Experimental

To 120 g. of poly phosphoric acid in a mechanically stirred flask is added a solution of 75 g. (0.50 mole) dinitropropanol in 30 ml. of toluene. The temperature is raised by steam bath to 60°C, and water pump vacuum pulled until all volatile material is removed. Then 55 g. (0.72 mole) of commercial glacial acrylic acid containing inhibitor is added and the temperature is maintained at 50-60°C. for three hours. The reaction mixture is stirred into water and the oil extracted twice with ether. After washing the combined ether layers successively with water, 2% sodium hydroxide, 4% sodium bisulfite, and water, the ether is removed and the product pulled dry by vacuum to obtain 73.5 g. (72% yield) of DNPA monomer.

TABLE I

<u>Run</u>	<u>DPL</u>	<u>Acrylic Acid</u>	<u>Poly Phosphoric Acid</u>	<u>Toluene</u>	<u>Yield</u>	<u>Polymer by Mass</u>
142	75 g.	48 g.	100 g.		24%	sol.
143	75	45	100		49	no run
146	75	43	100		poly.	
146A	75	43	75		poly.	
147	75 (Re-X)	43	150		35	no run
147A	75 (Re-X)	43	100		20	"
503	70 (Sub)	55	140		35	"
504	75 (Sub)	55	120	75 ml.	66	"
505	75	55	120	25 (removed)	72	"
506	164 (DBL)	110	250		poly.	
507	150	110	250	60	54	no run
508	150	110	250	60	65	Insol.
509	75	55	120		poly.	
510	75	55	120	30 (20 removed)	20 (steam distilled)	
511	150	110	240	30 benzene	50	Insol.
514	150	100	240	30	66	Insol.
monomer from 514 rewashed						Insol.

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10

Page 3

B. OXIDIZING AGENTS FOR NITROPARAFFIN SALTS

In our continual search for a reagent that will replace silver ion for the oxidation of the nitroparaffin salts in the presence of nitrite, several systems were tried. One that has been suggested is an oxidizing agent in the presence of silver. Using the sodium salt of 2-nitropropane in the presence of nitrite, one equivalent of silver ion and one equivalent of hydrogen peroxide did not yield any more dinitropropane than if the silver alone had been used. When ferric ion, or the complex ferricyanide, was used under the same conditions as the oxidative-nitration using silver, a 94% yield of 2-nitro-2-nitrosopropane was immediately precipitated.

C. DINITROBUTYL ACRYLATE

Dinitrobutanol was prepared in the standard oxidative-nitration procedure from fractionated 1-nitropropane in 81 and 87% yields. In one preparation after the precipitated silver had been washed twice, by slurring and filtering, and dissolved in nitric acid, an oil layer appeared. The layer was separated, washed, and distilled to obtain 40 g. of colorless product identified by nitrogen analysis and refractive index as dinitrobutanol. This amounts to 8.5% of the theoretical product and indicates the difficulty of washing the cake completely.

Dinitrobutyl acrylate was prepared by the acrylyl chloride-aluminum chloride procedure in 70 and 81% yields. The first run produced an insoluble polymer on bulk polymerization.

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10
Page 4

	<u>No. of Copies</u>		<u>No. of Copies</u>
Dept. of the Air Force Hq. USAF, DCS/D Washington 25, D.C. Attn: AFDRD-AN, Maj. H. R. Schmidt	1	Commanding General Redstone Arsenal Huntsville, Alabama Attn: Technical Library	2
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCEGH-2	1	Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: SI-5	1
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCLPN-2	1	Department of the Navy Bureau of Ordnance Washington 25, D.C. Attn: Ad3, Technical Library	1
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCLPN-2	1	Commanding Officer U.S. Naval Air Rocket Test Station Lake Denmark Dover, New Jersey Attn: Technical Library	1
Commanding General Wright Air Development Center Wright-Patterson Air Force Base Ohio Attn: WCLPN-2	1	Commanding Officer U. S. Naval Powder Factory Indian Head, Maryland Attn: Research and Development Department	2
Commanding General Aberdeen Proving Ground Maryland Attn: Ballistic Research Laboratories ORDBG-BLI	2	Commander U.S. Naval Ordnance Laboratory White Oak Silver Spring, Maryland Attn: Library	1
Commanding General Frankford Arsenal Bridge and Tacony Streets Philadelphia, Pennsylvania Attn: Pitman-Dunn Laboratory	1	Commander U.S. Naval Ordnance Test Station Inyokern, China Lake, California Attn: Technical Library Branch	3
Department of the Army Office, Chief of Ordnance Washington 25, D.C. Attn: ORDTU	1	Department of the Navy Office of Naval Research Washington 25, D.C. Attn: Code 429	3
Commanding Officer Office of Ordnance Research Box CM Duke Station Durham, North Carolina	1	Commanding Officer Office of Naval Research Branch Office 86 East Randolph Street Chicago 1, Illinois Attn: Lt. M. C. Laug	1
Commanding Officer Picatinny Arsenal Dover, New Jersey Attn: Library	2		

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10
Page 5

	<u>No. of Copies</u>		<u>No. of Copies</u>
Commanding Officer Office of Naval Research 1030 East Green Street Pasadena 1, California	1	Experiment, Incorporated P. O. Box 1-T Richmond 2, Virginia Attn: Librarian	1
Bureau of Aeronautics Representative c/o Aerojet-General Corporation Azusa, California	1	Hercules Experiment Station Wilmington, Delaware Attn: A. M. Ball	1
Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: TD-4	1	Director Jet Propulsion Laboratory 4800 Oak Grove Drive Pasadena 3, California	1
Aerojet-General Corporation P. O. Box 296 Azusa, California Attn: Librarian	2	Arthur D. Little, Inc. 30 Memorial Drive Cambridge 42, Massachusetts Attn: W. A. Sawyer	1
Allegany Ballistics Laboratory P. O. Box 270 Cumberland, Maryland	1	Arthur D. Little, Inc. 30 Memorial Drive Cambridge 42, Massachusetts Attn: E. L. Kreidl	1
Armour Research Foundation of Illinois Institute of Technology Technology Center Chicago 16, Illinois Attn: Propulsion and Structures Research; Department M	1	Naval Ordnance Research School of Chemistry University of Minnesota Minneapolis 14, Minnesota Attn: B. L. Crawford, Jr.	1
Atlantic Research Corporation 812 North Fairfax Street Alexandria, Virginia	1	National Fireworks Ordnance Corp. West Hanover, Massachusetts Attn: S. J. Porter	1
Bureau of Mines 4800 Forbes Street Pittsburgh 13, Pennsylvania Attn: Explosives and Physical Sciences Division	2	Ohio State University Research Foundation Columbus 10, Ohio Attn: Harold Shechter	1
Catholic University of America 7th St. and Michigan Ave., N.E. Washington 17, D.C. Attn: F. O. Rice	1	Logan E. Taylor, Security Representative Room 441, Adams Building Phillips Petroleum Company Bartlesville, Oklahoma Attn: Frances E. Varvel	1
E. I. du Pont de Nemours & Co. 10th and Market Streets Wilmington, Delaware Attn: W. F. Jackson	1	Project Squid Princeton University Princeton, New Jersey Attn: Librarian	1

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10
Page 6

	<u>No. of Copies</u>		<u>No. of Copies</u>
Purdue University Department of Chemistry Lafayette, Indiana Attn: Henry Feuer	1	B. F. Goodrich Company Research Center Brecksville, Ohio Attn: Vice President/Research	1
Rohm and Haas Company Redstone Arsenal Research Division Huntsville, Alabama Attn: Technical Director	1	Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: Aer 12-3 Contents only marked "For British Joint Services Mission"	4
Solid Propellant Information Agency Applied Physics Laboratory The Johns Hopkins University Silver Spring, Maryland Attn: P. K. Reilly, Jr.	8	Department of the Navy Bureau of Aeronautics Washington 25, D.C. Attn: Aer 12-3 Contents only marked "For Canadian Joint Staff"	4
Standard Oil Company Research Department P. O. Box 431 Whiting, Indiana Attn: W. H. Bahlke	1	Department of Chemistry Ohio State University Columbus 10, Ohio Attn: Elizabeth F. Riley	1
Thiokol Chemical Corporation Redstone Arsenal Huntsville, Alabama Attn: Technical Director	2	Explosives Division Naval Ordnance Laboratory White Oak Silver Spring 19, Maryland Attn: D. V. Sickman	1
Thiokol Chemical Corporation Elkton Division Elkton, Maryland Attn: D. W. Kershner	1	California Institute of Technology Pasadena, California Attn: E. R. Buchman	1
U. S. Rubber Company General Laboratories Market and South Streets Passaic, New Jersey Attn: P. O. Tawney	1	General Aniline & Film Corp. Central Research Laboratory Easton, Pennsylvania Attn: Joseph W. Lang	1
Western Cartridge Company East Alton, Illinois Attn: R. L. Womer	1	Department of Chemistry Purdue University Lafayette, Indiana Attn: G. B. Bachman	1
Reaction Motors, Inc. Rockaway, New Jersey Attn: Librarian	1	Bureau of Ordnance, Re2c Department of the Navy Washington 25, D.C. Attn: T. L. Brownyard	1
Phillips Petroleum Company P. O. Box 548 McGregor, Texas Attn: Librarian, J. Wiss	2		

CONFIDENTIAL

CONFIDENTIAL

COMMERCIAL SOLVENTS CORP.

Report No. Q-10
Page 7

	<u>No. of Copies</u>		<u>No. of Copies</u>
Department of Chemistry		Evans Research and Development Corp.	
George Washington University		250 East 43rd Street	
Washington, D. C.		New York 17, New York	
Attn: William F. Sager	1	Attn: E. J. Hewitt	1
Department of Chemistry		Los Alamos Scientific Laboratory	
University of Maryland		Los Alamos, New Mexico	
College Park, Maryland		Attn: Technical Library	2
Attn: N. L. Drake	1		
Commanding Officer		Ethyl Corporation	
Chemical Corps Chemical and		1600 West Eight Mile Road	
Radiological Laboratories		Ferndale 20	
Army Chemical Center, Maryland		Detroit, Michigan	
Attn: Technical Library	1	Attn: Roy Sugimoto	1

CONFIDENTIAL

UNCLASSIFIED

UNCLASSIFIED